

CXLVI.—*Diethylenetriamine and Triethylenetetramine.*

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THE interaction of ethylene dichloride and a large excess of ammonia has been investigated by Kraut (*Annalen*, 1882, **212**, 253), who considered that it led almost entirely to ethylenediamine, although the reaction of the alcohol-soluble portion of the mixed hydrochlorides with potassium bismuth iodide indicated that a small proportion of piperazine was formed.

The author had occasion to prepare several kilograms of ethylenediamine, essentially by Kraut's method, and it was thought to be of interest to investigate in more detail the other products of the reaction. The hydrochlorides obtained by evaporation of the product were converted into the corresponding bases and fractionally distilled. The portion of higher boiling point consisted mainly of diethylenetriamine, whilst there was also produced, although in much smaller quantity, triethylenetetramine. The intermediate

cyclic bases, piperazine and triethylenetriamine, appeared to be absent. Of the two bases isolated, the former was first obtained by Hofmann (*Proc. Roy. Soc.*, 1860, **10**, 619), admixed with triethylenetriamine, by the action of ammonia on ethylene dibromide, and was separated by the more sparing solubility of its platinichloride; the second base he obtained by the interaction of ethylenediamine and ethylene dibromide (*loc. cit.*), ethylene dibromide and alcoholic ammonia (*loc. cit.*), and ethylenediamine and ethylene dichloride (*Ber.*, 1890, **23**, 3712). For purposes of identification and characterisation, a number of derivatives of both have been prepared.

It is of interest to record that the direct union of ethylene with chlorine, utilised in the preparation of the ethylene dichloride required in the present experiments, shows that electrolytic chlorine from a freshly charged cylinder is considerably more active, under identical conditions, than that prepared from bleaching powder. This is in accordance with the view that chlorine is activated by exposure to an electric discharge (compare Kellner, *Zeitsch. Elektrochem.*, 1902, **8**, 500; Russ, *Monatsh.*, 1905, **26**, 627; Briner and Durand, *Zeitsch. Elektrochem.*, 1908, **14**, 706), and that chlorine prepared by electrolysis is more active towards hydrogen (Chapman and MacMahon, *T.*, 1909, **95**, 135).

Contrary to the experience of Russ (*Chem. Ind.*, 1908, **31**, 131), the increased activity is not lost by heating or by contact with water or solutions of such salts as calcium chloride or potassium chlorate. As an example, the fractionation of the products of two experiments may be cited, the results being representative of many others. In the first, using chlorine from bleaching powder, 92 per cent. of the product distilled between 84° and 88°, only 4 per cent. passing over at a higher temperature. In the second, using chlorine from a freshly charged cylinder, only 7 per cent. distilled between 80° and 90°, 25 per cent. passing over between 90° and 100°, 50 per cent. between 100° and 120°, and 14 per cent. above that temperature.

As an alternative to the Kraut process, the reduction of amino-acetonitrile was investigated. The catalytic reduction with hydrogen under pressure in the presence of nickel suboxide had already been claimed to yield ethylenediamine (Brit. Pat. 21883 of 1914). Reduction with sodium and alcohol, zinc and hydrochloric acid, and iron and hydrochloric acid also yielded ethylenediamine, although, as hydrolysis of the nitrile proceeded simultaneously, the yield never exceeded 33 per cent. of the theoretical.

## EXPERIMENTAL.

*Separation of the Bases.*

The bases obtained by distilling the mixed hydrochlorides with solid sodium hydroxide, preferably under somewhat diminished pressure, were freed from water by means of solid sodium hydroxide\* and then distilled, first under the ordinary pressure to remove most of the ethylenediamine hydrate, and then under 20 mm. There was first obtained a small fraction boiling below  $100^{\circ}$  which consisted almost entirely of ethylenediamine, and after this most of the remaining oil passed over between  $100^{\circ}$  and  $120^{\circ}$ . The temperature then rose to  $155^{\circ}$  without remaining constant at any intermediate point, and a fraction was collected boiling between  $155^{\circ}$  and  $165^{\circ}/20$  mm. The first fraction proved to consist almost entirely of diethylenetriamine, which distilled at  $109^{\circ}/20$  mm. The second fraction on redistillation boiled at  $157^{\circ}/20$  mm., and proved to be triethylenetetramine.

*Diethylenetriamine and its Derivatives.*

Diethylenetriamine dissolves in water with the evolution of heat and apparent formation of a hydrate. The aqueous solution of the base gives copious, white precipitates with potassium mercuri-iodide, mercuric chloride, or phosphotungstic acid, soluble in excess of the base, but no precipitate with tannic acid. It reduces silver nitrate on warming. The alcoholic solution yields an insoluble carbonate when treated with carbon dioxide. Attempts to titrate the base with standard acid, using methyl-orange, Congo-red, litmus, or cochineal as indicator, proved unsuccessful, as no definite end-point could be obtained. For analysis, it was finally distilled over a little solid sodium hydroxide, and was afterwards kept out of contact with moisture or carbon dioxide (Found: C=46.3; H=13.1; N=40.3. Calc.: C=46.6; H=12.7; N=40.75 per cent.).

The trihydrochloride (Hofmann, *Proc. Roy. Soc.*, 1862, **11**, 420) separates from aqueous alcohol containing excess of hydrogen chloride in bunches of feathery needles which melt at  $233^{\circ}$  (corr.), sintering from  $225^{\circ}$  (Found: Cl=50.1, 50.2; N=19.6. Calc.: Cl=50.1; N=19.8 per cent.).

The *tripicrate* is sparingly soluble, even in boiling water, and crystallises in glistening, flattened prisms which melt and decom-

\* It is not sufficient simply to distil over sodium hydroxide.



pose at  $212^{\circ}$  (corr.) (Found:  $N=21.5$ .  $C_4H_{13}N_3, 3C_6H_3O_7N_3$  requires  $N=21.3$  per cent.).

The *oxalate* crystallises from water, in which it is readily soluble, in flattened prisms containing  $4H_2O$ . After drying at  $110^{\circ}$ , it melts and effervesces at  $183^{\circ}$  (corr.) (Found: loss at  $110^{\circ}=13.0$ .  $2C_4H_{13}N_3, 3C_2H_2O_4, 4H_2O$  requires  $H_2O=13.1$  per cent. In dried substance,  $N=17.5$ .  $2C_4H_{13}N_3, 3C_2H_2O_4$  requires  $N=17.6$  per cent.).

The *citrate* is practically insoluble in alcohol, ether, or chloroform, but readily so in water, from which it separates in well-defined, rhombic prisms containing  $1H_2O$ . After drying at  $110^{\circ}$ , it melts and effervesces at  $206^{\circ}$ , sintering from  $200^{\circ}$  (Found: loss at  $110^{\circ}=6.3$ .  $C_4H_{13}N_3, C_6H_8O_7, H_2O$  requires  $H_2O=5.8$  per cent.). In dried substance,  $N=14.4$ .  $C_4H_{13}N_3, C_6H_8O_7$  requires  $N=14.2$  per cent.).

The *triacetyl* derivative is practically insoluble in alcohol or light petroleum, but very readily soluble in water. It separates from 70 per cent. alcohol as a felted mass of needles, which, in contact with the solvent, change to well-defined prisms melting at  $220^{\circ}$  (corr.) (Found:  $N=18.0$ .  $C_{10}H_{19}O_3N_3$  requires  $N=18.3$  per cent.).

The *tribenzoyl* derivative is very sparingly soluble in ether, or light petroleum, but readily so in water or alcohol. From chloroform it separates in small, flattened prisms containing one molecule of the solvent, which is gradually lost on exposure to the air, but regained on keeping over chloroform in a desiccator. After removal of the solvent of crystallisation, it melts at  $166^{\circ}$  (corr.) (Found:  $CHCl_3=21.9$ . After forty-eight hours, this had diminished to  $16.1$  per cent. In dried substance,  $C=71.9$ ;  $H=6.1$ ;  $N=10.1$ .  $C_{25}H_{25}O_3N_3$  requires  $C=72.2$ ;  $H=6.1$ ;  $N=10.1$  per cent.).

### *Triethylenetetramine and its Derivatives.*

Triethylenetetramine behaves very similarly to diethylenetriamine in its reactions, dissolving in water with evolution of heat, forming an insoluble carbonate when carbon dioxide is passed through its alcoholic solution, and giving precipitates with potassium mercuri-iodide, mercuric chloride, and phosphotungstic acid. It reduces silver nitrate on warming. For analysis, it was finally distilled over solid sodium hydroxide (Found:  $C=48.8$ ;  $H=12.7$ ;  $N=38.0$ . Calc.:  $C=49.3$ ;  $H=12.4$ ;  $N=38.3$  per cent.).

The tetrahydrochloride separates from 70 per cent. alcohol containing excess of hydrogen chloride in minute needles (Found:  $Cl=48.0$ . Calc.:  $Cl=48.5$  per cent.).

The *tetrapicrate* is very sparingly soluble, even in boiling water, from which it separates in fern-like clusters of minute, rhombic prisms melting and decomposing at  $240^{\circ}$  (corr.) (Found: N=20.7.  $C_6H_{18}N_4, 4C_6H_3O_7N_3$  requires N=21.1 per cent.).

The *hydrogen oxalate* is sparingly soluble in water, and separates in glistening needles, which effervesce at  $243^{\circ}$  (corr.) and contain  $1H_2O$  (Found: loss at  $110^{\circ}$ =3.0.  $1H_2O$  requires 3.2 per cent. In dried material, C=33.3; H=5.5; N=10.9.  $C_6H_{18}N_4, 4C_2H_2O_4$  requires C=33.2; H=5.2; N=11.1 per cent.).

The tetrabenzoyl derivative dissolves sparingly in water or alcohol, but readily in chloroform. It separates from a mixture of chloroform and alcohol in fine, powdery crystals melting at  $238^{\circ}$  (corr.) (Hofmann, *Ber.*, 1890, **23**, 3717, gives  $228-229^{\circ}$ ) (Found: C=72.8; H=6.5; N=9.9. Calc.: C=72.55; H=6.1; N=10.0 per cent.).

#### *Methyleneaminoacetonitrile and Aminoacetonitrile.*

Methyleneaminoacetonitrile was prepared substantially by the process described by Klages (*Ber.*, 1903, **36**, 1511). It was found, however, that the time of addition of the cyanide could be materially decreased without detriment to the yield so long as the temperature was maintained below  $10^{\circ}$  during the first half of the addition, and below  $15^{\circ}$  during the second. It was readily converted into aminoacetonitrile hydrochloride by shaking with the calculated quantity of *N*-alcoholic hydrogen chloride, the yield amounting to 90 per cent. of the theoretical.

#### *Reduction of Aminoacetonitrile Hydrochloride.*

*With Sodium and Alcohol.*—Twenty grams of the hydrochloride were added to 60 c.c. of alcohol in which 5 grams of sodium had previously been dissolved, 80 grams of sodium were added, and, after the first violent reaction had ceased, the mixture was heated on the water-bath, 250 c.c. of alcohol being gradually added. After about an hour, most of the alcohol was removed by distillation, a little 90 per cent. alcohol added to ensure that the sodium was all used, water added, and the mixture transferred to a copper flask and distilled to dryness under somewhat diminished pressure. The distillate was boiled to remove ammonia, neutralised with hydrochloric acid, and concentrated to crystallisation. The yield of ethylenediamine dihydrochloride varied from 25 to 33 per cent. of the theoretical.

*With Iron and Hydrochloric Acid.*—Five grams of aminoaceto-



nitrile hydrochloride were dissolved in 100 c.c. of water, 16 grams of iron filings added, and 50 c.c. of hydrochloric acid added slowly during an hour, with shaking. At the end of the reaction, the product was evaporated to dryness, distilled from a copper flask with sodium hydroxide, and the base in the distillate isolated as hydrochloride. The yield amounted to 10 per cent. of the theoretical.

*With Zinc and Hydrochloric Acid.*—To a solution of 6.8 grams of the hydrochloride in 100 c.c. of water, 30 grams of zinc were added, and 70 c.c. of concentrated hydrochloric acid added, as above, the product being then treated as in the previous reduction. The yield of ethylenediamine dihydrochloride amounted to 25 per cent. of the theoretical.

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